

(12) **UK Patent Application** (19) **GB** (11) **2 263 108** (13) **A**

(43) Date of A publication **14.07.1993**

(21) Application No **9200559.4**

(22) Date of filing **11.01.1992**

(71) Applicant  
**Albright & Wilson Limited**

**(Incorporated in the United Kingdom)**

**PO Box 3, 210-222 Hagley Road West, Oldbury,  
Warley, West Midlands, B68 0NN, United Kingdom**

(72) Inventors  
**Christopher David Imrie  
Robert Eric Talbot**

(74) Agent and/or Address for Service  
**Colin D Kinton  
Albright & Wilson Limited, Patents Department,  
PO Box 3, 210-222 Hagley Road West, Oldbury,  
Warley, West Midlands, B68 0NN, United Kingdom**

(51) INT CL<sup>5</sup>  
**C01B 11/02 11/20**

(52) UK CL (Edition L)  
**C1A A9  
U1S S1250 S1304 S1307 S1400**

(56) Documents cited  
**GB 1448337 A GB 0675541 A**

(58) Field of search  
**UK CL (Edition K) C1A A16 A18 A8 A9  
INT CL<sup>5</sup> C01B  
Online databases: WPI, CLAIMS**

(54) **Halogen oxides in aqueous solution**

(57) Halogen oxides in aqueous solution can be made by reacting solid, active halogen precursors with an aqueous medium. In particular, chlorine dioxide can be made by passing sodium chlorite or sodium chlorate through a vessel containing an active halogen source, e.g. chlorine-release tablets.

These may be 'rapid release' eg sodium dichloro isocyanurate dihydrate or 'slow release' eg trichloro isocyanuric acid.

**GB 2 263 108 A**

**HALOGEN OXIDES IN AQUEOUS SOLUTION**

This invention relates to a method for the production of halogen oxides in aqueous solution and to aqueous solutions of halogen oxides obtained thereby.

While the present invention will hereinafter be described with particular reference to chlorine dioxide, it is not to be construed as being limited thereto.

Chlorine dioxide is widely used for, inter alia, the treatment of effluent or process waters and for addition to water systems (for example, as a biocide). Since gaseous chlorine dioxide tends to be explosive, aqueous solutions of chlorine dioxide are used for most commercial purposes.

Conventional methods of generating solutions of chlorine dioxide involve adding chlorine and/or acid to chlorite or chlorate solutions. The chlorine may be added, for example as sodium hypochlorite solution. This may be achieved in one of a variety of generators.

These conventional methods involve the handling of two or more solutions which need to be metered in to the generator. Some of the solutions, such as sodium hypochlorite, are in themselves quite hazardous. Also, it is hazardous to handle chlorine gas.

We have now found that chlorine dioxide can be produced by passing a solution of sodium chlorite or sodium chlorate through a vessel containing an active halogen source, for example chlorine-release tablets. These chlorine-release tablets may be trichlor-isocyanuric acid or sodium dichloro-isocyanurate; the former is slow-dissolving and would best be used where a steady, continuous treatment is required, while the latter is quick-dissolving and would best be used where a "shot" dose of chlorine dioxide is to be generated.

Accordingly, the present invention provides a method for the production of one or more halogen oxides in aqueous solution, said method comprising the reaction of an active halogen source in solid form with an aqueous medium.

The present invention also provides an aqueous solution of one or more halogen oxides produced by the method described in the immediately preceding paragraph.

Preferably, the active halogen source is in the form of tablets or briquettes. Alternatively, the active halogen source may be in the form of a powder or granules.

In one preferred embodiment of the present invention, the active halogen source is a source of chlorine. Such a source may be a "rapid-release" or a "slow-release" source.

An example of a "rapid-release" source of chlorine is sodium dichloro-isocyanurate dihydrate, available from Chlor-Chem Limited as Fi-CLOR CLEARON.

An example of a "slow-release" source of chlorine is trichloro-isocyanuric acid, available from Chlor-Chem Limited as Fi-CLOR 91.

(The words Fi-CLOR and CLEARON are Registered Trade Marks).

In an alternative embodiment of the present invention, the active halogen source is a source of chlorine and bromine. An example of such a source is bromochloro-dimethyl-hydantoin, available from Great Lakes Chemical Corporation as BROMICIDE (Registered Trade Mark).

Preferably, the active halogen source, in the form of tablets or briquettes, is packed into a vessel (e.g. a tower), provided with means to allow the flow therethrough of an aqueous medium.

The aqueous medium may comprise a metal chlorite, for example sodium chlorite, in aqueous solution. Suitably, the aqueous solution contains an effective amount of up to 40% by weight of the sodium chlorite.

Alternatively, the aqueous medium may comprise a metal bromite, a metal bromate or a metal chlorate in aqueous solution.

Again alternatively, the aqueous medium may comprise a stabilised aqueous solution of chlorine dioxide. A suitable example of this is available from Rio Linda Company as DURAKLOR (Registered Trade Mark).

Preferably, the reaction between the aqueous medium and the active halogen source takes place under acid-to-neutral conditions.

Halogen oxide solutions produced according to the present invention are especially suitable for use in connection with small water-cooling systems.

Other applications include, but are not limited to, the following:

Bleaching of paper in paper mills;

As a biocide in water treatment (for the control of bacteria, algae, fungi, viruses, protoza and the like);

Effluent treatment;

Removal of iron and manganese from water;

Control of taste, odour and colour in water;

Control of odour in foul air;

Sterilisation of air (e.g. in operating theatres);

Use in sterilisation of surfaces in foam generators;

Food processing;

Reclaiming waste water;

Treatment of "sour water" to remove hydrogen sulphide, e.g. in oil production;

Leather processing;  
Electronics applications;  
Beet processing.

Chlorine dioxide has many advantages as compared to chlorine in that, unlike chlorine, it does not produce trihalomethanes (THM); it reduces the level of THM precursors and therefore can be used as a water pre-treatment; it is not, as regards its biocidal activity, sensitive to pH, and finally does not interact with ammonia or other nitrogenous compounds.

**CLAIMS**

1. A method for the production of one or more halogen oxides in aqueous solution, said method comprising the reaction of an active halogen source in solid form with an aqueous medium.
2. A method according to Claim 1, in which the active halogen source is in the form of tablets or briquettes.
3. A method according to Claim 1, in which the active halogen source is in the form of a powder or granules.
4. A method according to Claim 1, 2 or 3, in which the active halogen source is contained in a vessel provided with means to allow the flow therethrough of the aqueous medium.
5. A method according to any one of Claims 1 to 4, in which the active halogen source is a source of chlorine.
6. A method according to any one of Claims 1 to 4, in which the active halogen source is a source of chlorine and bromine.
7. A method according to any one of Claims 1 to 5, in which the active halogen source is a rapid-release source of chlorine.
8. A method according to any one of Claims 1 to 5, in which the active halogen source is a slow-release source of chlorine.
9. A method according to Claim 7, in which the active halogen source consists substantially of sodium dichloro-isocyanurate dihydrate.

10. A method according to Claim 8, in which the active halogen source consists substantially of trichlor-isocyanuric acid.
11. A method according to Claim 6, in which the active halogen source consists substantially of bromochloro-dimethyl-hydantoin.
12. A method according to any one of the preceding claims, in which the aqueous medium comprises a metal chlorite in aqueous solution.
13. A method according to Claim 12, in which the aqueous medium comprises sodium chlorite in aqueous solution.
14. A method according to Claim 12 or 13, in which the aqueous medium comprises an effective amount of up to 40% by weight sodium chlorite in aqueous solution.
15. A method according to any one of Claims 1 to 11, in which the aqueous medium comprises a metal bromite, a metal bromate or a metal chlorate in aqueous solution.
16. A method to any one of Claims 1 to 11, in which the aqueous medium comprises a stabilised aqueous solution of chlorine dioxide.
17. A method according to any one of the preceding claims, in which the reaction takes place under acid-to-neutral conditions.
18. An aqueous solution of one or more halogen oxides produced by the method of any one of Claims 1 to 17.

**Patents Act 1977**  
**Examiner's report to the Comptroller under**  
**Section 17 (The Search Report)**

Application number

9200559.4

**Relevant Technical fields**

(i) UK Cl (Edition K ) C1A (A8,A9,A16,A18)

(ii) Int Cl (Edition 5 ) C01B

Search Examiner

C A CLARKE

**Databases (see over)**

(i) UK Patent Office

(ii)  
 ON LINE DATABASES: WPI, CLAIMS

Date of Search

17 MARCH 1992

Documents considered relevant following a search in respect of claims

1 TO 18

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	GB 1448337 (KEMANORD) See Claim 1	1,3,5, at least
X	GB 675541 (NOVADEL-AGENE) See page 2 lines 102-128	1

SF2(p)

kg - c:\wp51\doc99\fil000822



Category	Identity of document and relevant passages	Relevant to claim(s)

### Categories of documents

**X:** Document indicating lack of novelty or of inventive step.

**Y:** Document indicating lack of inventive step if combined with one or more other documents of the same category.

**A:** Document indicating technological background and/or state of the art.

**P:** Document published on or after the declared priority date but before the filing date of the present application.

**E:** Patent document published on or after, but with priority date earlier than, the filing date of the present application.

**&:** Member of the same patent family, corresponding document.

**Databases:** The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).